Conversion of Ligno-cellulosic Biomass Waste into Cellulose Nano-Fibril (CNF) Biodegradable Film for Bioactive Food Packaging

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Abstract

Indonesia is rich in tropical fruit. However, many tropical fruits face a post-harvesting problem related to the short shelf-life of fruits due to the high respiration, transpiration, and decaying by fungi. To solve this problem, it is necessary to prolong the shelf-life of tropical fruit by applying bioactive food packaging which can prevent fruit from decaying and rotting. Among the prospective bioactive food packaging is biodegradable film made of cellulose nanofibril (CNF). CNF is new nanomaterial containing thin fiber from cellulose. This material forms transparent gel, thus it is easily to be modified into biodegradable film which is homogenous, safe, environmentally friendly, and renewable. CNF nanomaterial can be derived from lingo-cellulosic material through the process of lingo-cellullose degradation followed by homogenization using fluidization process. This process results in CNF transparent gel which can be readily modified as biodegradable film. This biodegradable film is then can be applied to the tropical fruits to prolong their shelf-life. CNF bioactive food packaging has high mechanical strength and high protection against oxidation process. This paper comprehensively reviews the advanced technology of upgrading lingo-cellulosic biomass waste into CNF biodegradable film and the technic of applying it as bioactive fruit packaging.

Keywords: *Cellulose nanofibril, transparent gel, tropical fruits, rotting, shelf-life*

Introduction

Indonesia is an agricultural country and rich in agricultural products, such as vegetables and fruits. Among the high-value product of agricultural commodities is tropical fruits. Indonesia has 12 varieties of tropical fruits which are identified as Indonesia’s exotic and native fruits, they are: keprok oranges, durians, papayas, bananas, watermelon, melon, mangosteens, mangoes, pineapples, avocado, rambutans, and salaks. Those kinds of fruits have great prospect for national sales as well as for export market outside the country. In fact, Indonesia is also potential to be the major producer and exporter of tropical fruits in South East Asia region. For example, currently, Indonesia is the world’s largest producer and exporter of salaks fruit. Salaks production in Indonesia has increased from 423.5 ton in 2000 to 862.5 ton in 2009. Fresh salak fruit has been exported to China, Hongkong, Singapura, dan Middle East, and the export will be expanded to Australia, Europe, and Japan. Salaks is also supplied from Yogyakarta city to other cities and islands of Indonesia (Lestari et al., 2013). To establish export performance, improvement in competitiveness of the agricultural commodities is crucial.

Among the key factor of tropical fruits export is the freshness and quality of the fruit (Tih and Jani, 2010). However, many Indonesian tropical fruits including Salak face a post-harvesting problem related to the short shelf-life of fruits due to the high respiration and transpiration, and decaying by fungi. Most fruits contain high amount of water (more than 80%). This condition makes the fruits unpreserved. Fruits are comprising living tissues which causes the fruits cannot endure under the stresses of time, temperature, inappropriate harvesting and post-harvesting system, as well as poor transportation and storage (Chong and Low, 2010). Furthermore, the damage on the fruits skin also enable the growth of microbe which will increase respiration rate, heat production, and the decay. The fast decaying of fruit will result in poor marketability. To solve this problem, it is necessary to prolong the shelf-life of tropical fruit by applying bioactive food packaging. Bioactive food packaging can prevent fruit from decaying and rotting.

Among the prospective and eco-friendly bioactive food packaging is biodegradable film made of cellulose nanofibril (CNF). CNF is new nanomaterial containing thin fiber from cellulose with the size of 5-50nm. In low concentration, this material forms transparent gel, thus it is easily to be modified into biodegradable film which is homogenous, safe, environmentally friendly, and renewable. CNF nanomaterial can be derived from lingo-cellulosic material through the process of lingo-cellullose degradation followed by homogenization using fluidization process.

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This process result in CNF transparent gel which can be readily modified as biodegradable film. CNF biodegradable film is then can be applied to the tropical fruits to protect them from rotting by spray coating or immersion method. This paper will comprehensively review the advanced technology of upgrading ligno-cellulosic biomass waste into CNF biodegradable film and the technic of applying it as bioactive fruit packaging.

Cellulose

Cellulose is the most plentiful polymer on earth. It is a kind of highly stable polymer consisting of glucose and attached with linear chains up to 12,000 residues. Cellulose is mainly composed of (1,4)-d-glucopyranose units, which are attached by β-1,4 linkages. The average molecular weight is around 100,000. Cellulose molecules are highly insoluble in most organic solvents. Cellulose molecules is a package made of micro-fibrils, which consists of crystalline and amorphous regions. Chemical formula of cellulose is $(C_6H_{10}O_5)_n$ (Vercoe et al., 2005). Cellulose material is usually found as part of plant biomass. All plant materials are mostly composed of three major units *i.e.*, cellulose (40-50%), hemicellulose (20-30%) and lignin (10-25%). Cellulose is a major structural component of plant cell walls, which is responsible for mechanical strength, while, hemicellulose macromolecules are often repeated polymers of pentoses and hexoses. Lignin contains three aromatic alcohols (coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol) and forms a protective seal around the other two components *i.e.*, cellulose and hemicelluloses (Menon and Rao, 2012). The structure of lingo-cellulosic biomass is demonstrated in Figure 1.

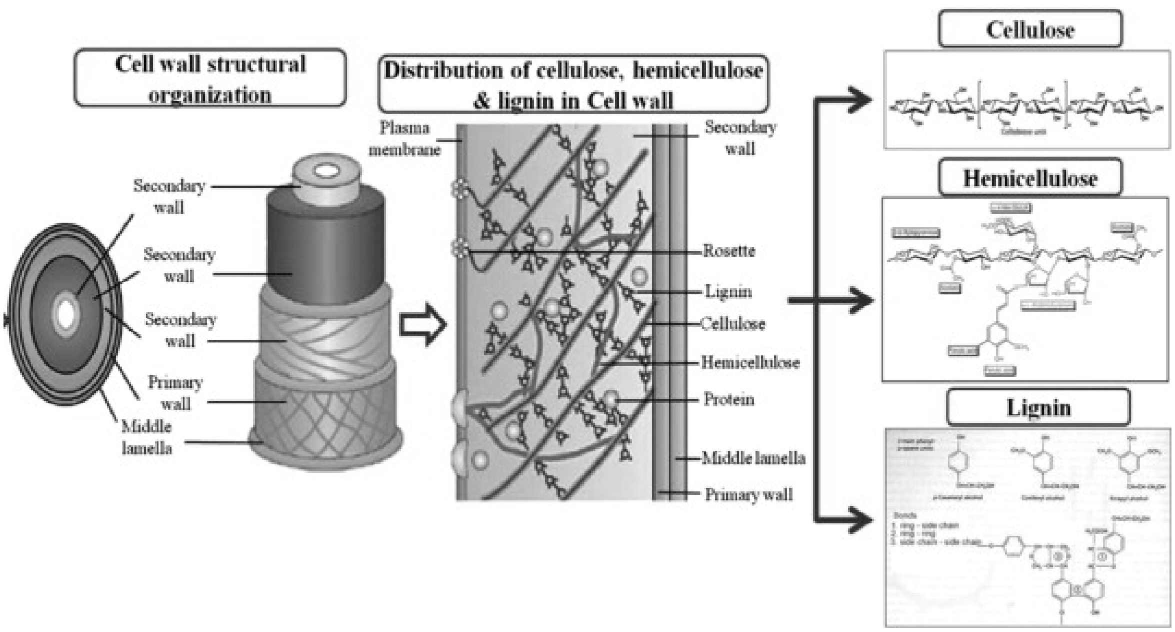

Figure 1. Structures of Lignocellulosic Biomass (Menon and Rao, 2012)

Cellulose is abundant in Indonesia since Indonesia is a major producer of agricultural products and 30% of Indonesia land is used for agriculture purpose. All agricultural biomass waste such as forestry and agro residue are composed of ligno-cellulosic materials. The abundant amount of agricultural biomass waste commonly remain unutilized. However, recently, lingo-cellulosic biomass has gained increasing interests and importance among the researcher because of their low price and renewable character, and their possibility to be converted into valuable products and value added chemicals (Anwar et al., 2014).

Cellulose has unique character. This polymer is consists of glucose-glucose linkages which are orderly in linear chains. The arrangement shows that C-1 of every glucose unit is bonded to C-4 of the next glucose molecule (Figure 2). These chains develop a fibrous structures called nanofibrils, which have size of 2 to 20 nm wide. These nanofibers form the structure of plants, some fungi, animals, and bacteria. These cellulosic nano-dimensional units crystalline regions, which causes the unique properties of cellulosic material such as: strength properties and piezoelectric properties equivalent to quartz. Cellulosic materials are uniform in size and shape, having self-assembly properties, and can also be modified to yield photonic structures. Thus, cellulosic material is prospective to be upgraded into cellulosic nanomaterial, which is the important platform material of various valuable products. In recent times, cellulosic nanomaterial is called as sustainable materials of choice for the 21th century (Postek et al., 2013).

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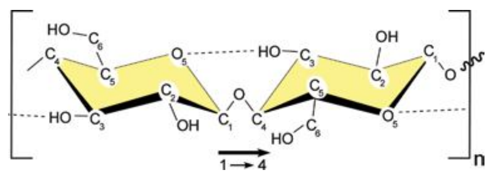

Figure 2. Structures of Cellulose Materials (Postek et al., 2013)

Cellulose Nanofibrils (CNF)

Cellulosic nanomaterial is recently recognized as the future green material. Hence, many research are conducted to develop commercialization of cellulosic nanomaterial. To date, there are many different types of cellulosic nanomaterial. The most popular are cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF). Cellulose nanocrystals are rod-like particle types and entirely made up of nanodimensional cellulose crystals. On the other hand, cellulose nanofibrils are fibril-like particle types comprising the regions of crystalline and amorphous cellulose. Cellulose nanofibrils (CNF) is also called as nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC) or cellulose nanofibers (Nechyporchuk et al., 2015).

CNF is a new cellulosic material and it can be synthesized from ligno-cellulosic biomass through several methods. The main procedure of CNF manufacturing is cellulose purification-mechanical pretreatment-biological/ chemical pretreatment-principal mechanical treatment to produce CNF-post treatment. The initial step is cellulose purification. At this stage, delignification process is carried out to separate lignin from the biomass material. Delignification can be performed through the cooking and bleaching process. Purified cellulose is then pulped. Pulping process can be performed by adding water to purified biomass until the concentration of solid content is 10 wt%. The mixture is then pulped by adding with 5 wt% of NaOH solution. The mixture of biomass and NaOH is then stirred for 2 hours at the temperature of 70-80 □. This process is run three times to well tailor the fibers. The resulted fibers are purified by using filtration process, followed by washing with distilled water. Bleaching process using $NaClO_2$ can also be managed if it is necessary (Boufi and Chaker, 2016).

The second step is cellulose pulp pretreatment by using mechanical process such as grinding, blending, and refining. This step is followed by the third step, i.e. biological/ chemical pretreatment, such as: 1) enzymatic hydrolysis of cellulose in the presence of cellulase enzyme to improve fibrillation process, 2) Carboxylation via TEMPO-mediated oxidation. In this process, 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) radical is used for selective oxidation of cellulose. The reaction involves conversion of the primary alcohol groups of cellulose into aldehydes and the oxidation of aldehydes to carboxylic groups as exhibited in Figure 3. This process results in CNF with the average individual width of 3-5 nm, 3) Carboxylation via periodate–chlorite oxidation of cellulose. This technique is employed to transform cellulose secondary, 4) Carboxymethylation, 5) Sulfonation. It is the way in which negative charged group is introduced to improve the fibrillation process. Sulfonation results in CNF with the average width of 10-60 nm (Nechyporchuk et al., 2015).

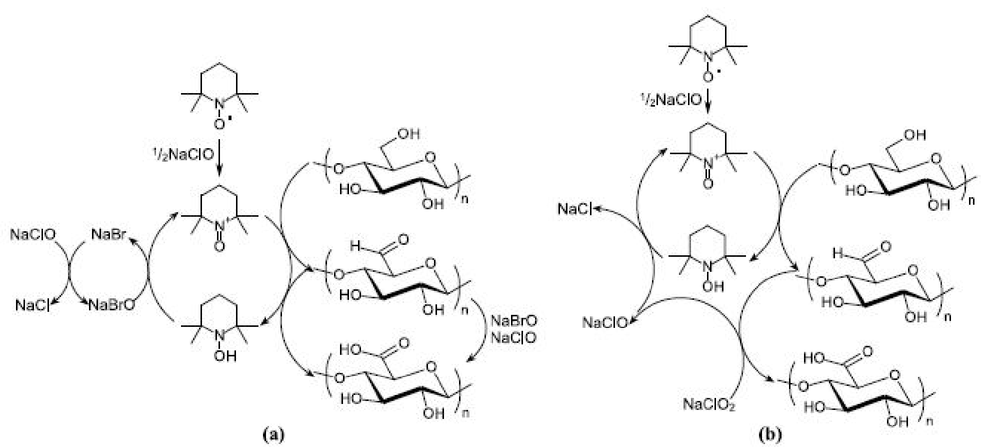

Figure 3. Carboxylation via TEMPO-mediated oxidation

Next step is the main mechanical process, which is designed with the purpose to break cellulose into small fragments of CNF. The common conventional methods of mechanical process are homogenization, grinding,

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blending, refining, and extrusion. On the other hand, some unconventional techniques have also been introduced such as ultrasonication and steam explosion. The common high pressure homogenization is applied using homogenizer and microfluidizer. From this process, CNF with individual diameter of less than 100 nm are yielded. Grinding is employed using ultra-fine friction grinding technique. This method yields CNF with the individual diameter of 20-90 nm. Refining process is the other method of mechanical process. The objective of refining process is to enlarge the fiber's cell wall which leads to the higher specific surface and volume of fibers. The higher surface and the volume of the microfibril, the easier it is to be accessed for the further process. Blending is usually performed using high speed blender (Boufi and Chaker, 2015). Based on this method, CNF with the individual diameter of 15-20 nm can be obtained.

The final step of CNF production is post-treatments. This process aims at surface chemical modification to obtain specific properties of CNF or to improve the quality of CNF.

There are many possible combinations of methods to produce CNF. Some popular procedures of operations are, for examples:

1. Mechanical pretreatment via refining method, followed by enzymatic hydrolysis as chemical pretreatment, and finally the principle mechanical process of CNF is conducted by refining and homogenization technique.
2. TEMPO-Mediated oxidation as chemical pretreatment followed by blending or homogenization to produce CNF
3. Carboxymethylation as chemical pretreatment, followed by homogenization as the principle process of CNF production

The different procedure of CNF production will result in the different properties of CNF, such as dimension, amount of fiber fragment, surface chemistry, crystallinity, and so on. CNF can be produced in various forms of products such as powder, suspension, film, hydrogel, and aerogel or porous sponge-like material. Figure 4 exhibits the visual appearance of CNF gel, which was produced through delignification followed by TEMPO-mediated oxidation pretreatment and mechanical blending to disintegrate fibril from cellulose. CNF has numerous possibilities of applications in industrial areas, for example: paper, packaging, concrete, oil drilling, cosmetics, drug delivery, food, and composite.

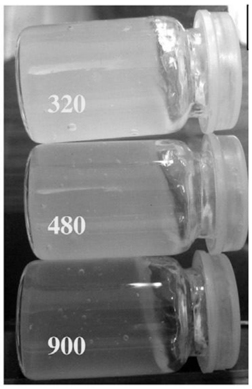

Figure 4. CNF Gel Produced by the Method of Delignification Followed TEMPO-Mediated Oxidation Pre-treatment, and Blending Using High Speed Blender (Boufi and Chaker, 2015).

Cellulose Nanofibril (CNF) for Food Packaging

CNF is a kind of bio-nanocomposite derived from biopolymer (cellulose). CNF can be modified into various forms such as gel, powder, and film. CNF film is applicable for several industrial purposes such as food packaging and drug delivery system.

Among the strategic application of CNF in industry is the development of CNF-based food packaging. The demand of high quality, economical, and environmental-friendly food packaging is fast growing due to the increasing needs of shelf extension of package food products and fruits. As the material for food packaging, CNF film holds many advantages since it is renewable, biodegrable, biocompatible, and low toxic. It is also has a unique gel forming characteristic (Deepa et al., 2016). One important key factor of food packaging quality is mechanical strength and barriers properties. Usually, biopolymer has poor mechanical and barriers properties. However, by forming cellulose biopolymer into nano-size composite material (CNF), it is easy to modify and enhance its properties. Compared to conventional biopolymer materials, CNF shows excellent properties such as low density, low thermal expansion, and outstanding mechanical properties, which make them relevant in various application. CNF is readily to be utilized as coat packaging material which provides biodegradable barriers with appropriate oxygen permeability. CNF coating is also ready to modify to obtain bioactive characteristic which will preserve food products from bacteria attack (Sudaram et al., 2016).

The excellence characteristic of CNF film makes this nano-biopolymer suitable to be applied as bioactive packaging for Indonesian tropical fruits. As tropical fruit packaging, CNF characteristic can be improved by using plasticizer such as sorbitol, glycerol, and mannitol, or modified using alginate (Deepa, 20116). To enhance its anti-microbial characteristic, CNF biodegradable film can be formulated with essential oil such as ginger, galangal, and turmeric oils. The application of CNF bioactive food packaging of tropical fruit is technically easy by spraying or dyeing. CNF food coating is prospective for prolong the shelf-life of tropical fruits.

Conclusion

Indonesia agricultural biomass waste is potential to be upgraded into nano biopolymer material called Cellulose Nanofibril (CNF). The process involves mechanical and chemical pretreatment, main mechanical process to disintegrate cellulose to CNF, and post-treatment for modifying CNF properties. CNF film has excellent mechanical strength and barriers which is potential for protecting tropical fruit from decay. Therefore, CNF film is prospective to be applied for prolonging the shelf-life of Indonesian tropical fruits.

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Lembar Tanya Jawab
Moderator: Kartika Udyani (Teknik Kimia ITATS Surabaya)

1.	Penanya	:	Kartika Udyani (Teknik Kimia ITATS Surabaya)
	Pertanyaan	:	- Teknik pencelupan dan spray mana yang baik?
			- Apakah tidak merusak apabila digunakan suhu 60℃
	Jawaban	:	- Lebih baik digunakan spraying. Pada udara panas.
			- Suhu medium
			- Belum diamati apakah merusak buah-buahan atau tidak
2.	Penanya	:	Bambang Sugiarto (Teknik Kimia UPN "Veteran" Yogyakarta)
	Pertanyaan	:	- spray pada suhu 60℃, akan berpengaruh tehadap proses pematanagan serta tingkat kematangan dari buah yang akan dispray?
	Jawaban	:	- Dry food/segar
			- Buah yang diteliti dalam kondisi segar (belum diteliti kualitas buah akibat spray, rusak atau tidak)
			- Buah yang diteliti yaitu salak.
	Saran	:	Suhu rendah dengan proses vakum dan sebelum dicoating diberi gas N_2